Synthesis and Characterization of Ni and Mn doped Co_3O_4 Thin Films for Electrochemical Supercapacitor Applications

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Ph.D. Synopsis

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Abstract of proposed work plan/problem:

In the present research work, Chemical deposition method will be used to synthesize Ni and Mn doped Co_3O_4 thin films on amorphous and fluorine doped tin oxide coated conducting glass substrates. Various characterization techniques such as XRD, SEM, FESEM, EDAX, UV-Visible spectroscopy, and DC electrical conductivity measurements will be used to study the structural, morphological, compositional, optical, and electrical properties of Ni and Mn doped Co_3O_4 thin films. Cyclic voltammogram, galvanostatic charge-discharge, and electrochemical impedance spectroscopy measurements will be used to study the electrochemical supercapacitor performance of the Ni and Mn doped Co_3O_4 thin films.

1. Introduction

In recent years, the demand for the renewable energy and energy storage conversion has increased because of reduction of fossil fuels and increased enthusiasm for the use of different electronic devices[1]. Our society is facing severe problems related to the small-scale energy storage. The rapidly growing population and unstructured industrialization pose a serious threat to future energy demand and environmental health [2]. Conventional energy sources are on the verge of their demise. hence significant progress is being made in discovering reliable energy sources and their storage technology, hence there is a search of clean energy sources and development of efficient designs for energy harvesting and storage had become of utmost importance[3].

The electrochemical capacitor or the supercapacitor emerged as a potentially important energy storage device that offers several advantages including high power density, fast charging/discharge rates, long cycle lifetime, wide range of operating temperature, environmental friendliness and safety. these features are expected to place ECs in the list of important solutions for future energy management and the provisions of high pulse energy needed for a variety of application [3-4].

Cobalt oxide Co_3O_4 is a promising material for different application such as optical smart windows, display devices, pigments for glass and ceramics, gas

sensors, solid state sensors, magnetic material catalysts, anode material for rechargeable Li-ion batteries, electrochromic devices, electro chemical systems and high temperature solar selective absorbers [4]. Co_3O_4 emerged as a good candidate as it adsorbs more-light even at high solar temperature and used for optoelectrical devices. Since the nanostructured Co_3O_4 thin film is good optical nonlinearity that can be applied for optical recording media having high recording density [5].

Transition metal oxides are promising electrode materials due to their higher theoretical capacitance and superior capacitive behavior. Tricobalt tetroxide (Co_3O_4) belongs to the spinel structure AB_2O_4 with Co^{2+} ions in the tetrahedral site and Co^{3+} ions in the octahedral site of the cubic closed pack lattice [2-6].It is a p-type semiconductor that has been widely used as a supercapacitor, heterogeneous catalyst, anode material in lithium-ion batteries, gas sensor, and solar energy absorber, where their properties are dependent on their morphology and size. The electrochemical performance of oxide materials depends mainly on the surface area, active surface sites, defects, and electrical conductivity.

In present study thin films will be deposited by using chemical route method. The various film properties like crystal structure, morphology, and optical, electrical and electrochemical properties will be studied. The results obtained will be compared and discussed.

2. Review of Literature and Development in the Subject:

Xue et al. [1] studied A composite electrode containing Co_3O_4 nanowire arrays, ultrathin MnO_2 nanosheets and Nano-flake-like Co $(OH)_2$ thin films was prepared through simple hydrothermal method combined with suitable heat treatment and electro-deposition. The Co_3O_4 nanowire was connected to MnO_2 nanosheets, and the Co $(OH)_2$ nanosheets were coated on the MnO_2 to form a complete network. The composite electrode showed a high specific capacitance of 3022.2 F/g at a current density of 10 A/g, and a satisfactory cyclic stability with 87.9% capacitance retention after 5000 cycles. An asymmetric electrode with Co_3O_4/MnO_2/Co $(OH)_2$ as the anode and activated carbon as the cathode was assembled by using 1 M KOH as electrolyte.

Samatha K and coworkers [7] used Cobalt oxide-based spinels in the form of Co_3O_4, $NiCo_2O_4$ and $ZnCo_2O_4$ are synthesized by the co-precipitation technique.

Powder X-ray diffraction studies confirm the arrangement of ions in spinel structure with minor secondary phases of native oxides. Scanning electron micrographs of spinels show the formation of fine nanostructures with an overall grain size below 90 nm for Co_3O_4 and $ZnCo_2O_4$. the grain size of $NiCo_2O_4$ varied from 100 to 250 nm.

Sidra Aslam et al [8] used a facile co-precipitation technique to synthesize transition metal (Ni, Mn, and Zn) doped Co_3O_4 material. X-ray diffraction analysis revealed the face-centered cubic lattice of Co_3O_4 with slight variation in lattice parameters. Densely packed spherical grains of pure Co_3O_4 with an average grain size of 50 nm were observed. However, the incorporation of a nominal amount of Ni, Mn, and Zn at Co-site resulted in a favorable porous morphology. The increasing porosity with substitution and presence of constituent elements was noticed from the scanning electron microscope and elemental mapping, respectively. Electrochemical measurements including cyclic voltammetry, galvanostatic charge-discharge curves, and electrochemical impedance spectroscopy were also performed.

N H Zaki [9]and coworkers reported the structural and electronic properties of the nickel (Ni) substitution on the cobalt oxide (Co_3O_4) to produce nickel cobaltite ($NiCo_2O_4$) using generalized gradient approximation + U parameter (GGA + U) calculation method. The spinel $NiCo_2O_4$ with half-metallic behavior has a relatively small band gap ~0.64eV which is spotted decreased from pure Co_3O_4 band gap 1.26eV. This is due to nickel doping decreased the band gap which also implies that an increase in electrical conductivity. Owing to good electrical conductivity, $NiCo_2O_4$ thus enables to be considered for application in supercapacitor. Analysis of the partial density of states (PDOS) showed the differences contributions of cobalt (Co) at the tetrahedral site (Td) and Ni at the conduction bands: Co (Td) ions not affected the majority spin which was in contrast with Ni ions.

S Lavanya and coworkers [10] deal with pure and 2, 4, 6, 8, and 10 wt.% Ni-doped Co_3O_4 thin films prepared using the Nebulizer spray pyrolysis method. An in-depth discussion was provided on improving crystalline, morphological, optical, electrical, and photodetection characteristics of pure and Ni-doped samples. The cubic spinel structure of Co_3O_4 was established by the X-ray diffraction (XRD) study. Microscopy studies using Field Emission Scanning

Electron (FESEM) technology reveal tiny grains aggregated together that were in qualitative accord with the crystalline sizes determined by XRD analysis. Energy dispersive X-ray (EDX) analysis was observed the presence of constituent elements in the prepared films. The results of the photoluminescence (PL) experiments demonstrate the quality of the crystal structure and the presence of defects in the films. According to the absorption measurements, two-band gap values were determined in the range of 1.55 to 1.25 eV and in the range of 2.0 to 2.0 eV for different Ni doping concentrations, respectively. The maximum photoconductive parameters such as photo-responsivity (R), external quantum efficiency (EQE), and detectivity (D*) of $1.64 \times 10^{-1} AW^{-1}$, 38%, and 9.273×10^{8} Jones were achieved for 8% Ni-doped Co_3O_4 sample. The results obtained in the present study indicate that the 8% Ni-doped Co_3O_4 sample finds suitable material.

Abdelhak Lekehal [11]et al presented the results of an experimental work devoted to the synthesis and the characterization of cobalt oxide (Co_3O_4) thin layers doped with transition metal (TM = Ni, Mn, Cu) in order to investigate their structural, optical and electrical properties. The materials were synthesized by the sol–gel method and deposited by dip-coating process. The synthesized samples were characterized by Ultraviolet-visible spectroscopy (UV–visible), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and Complex impedance spectroscopy to elucidate the optical, structural, vibrational and electrical properties. Our structural results show that the materials kept their cubic spinel structure with preferred orientation of (311), Our optical results show that the transmittance of all doped samples decreases compared to undoped Co_3O_4 and the doping leads to a reduction of their band gap energies. The complementary phase information is provided by FT-IR spectroscopy. FT-IR spectra of TM-doped Co_3O_4 confirms the presence of Co^{2+}–O and Co^{3+}–O vibrations in the spinel lattice. The Nyquist plots suggest that the equivalent circuits (parallel circuit of Rp and Cp) of our films are not qualitatively affected by the doping, but it was found that the effective resistance Rp decreases whereas the effective capacitance Cp increases with doping.

Congcong lu and coworkers [12] revived Supercapacitors which have been widely used in portable electronics and hybrid electric vehicles are considered to be fascinating energy storage devices owing to their higher energy density than

traditional capacitors and higher power density than batteries. The performance of supercapacitors is much dependent on the properties of the used electrode materials, and much effort has been devoted to exploring high-performance electrodes. During the past decade, cobalt-based materials, especially Co_3O_4 and its composites, have been regarded as prominent electrode materials for supercapacitors in view of their relatively low cost, high theoretical specific capacitance, non-toxicity, and excellent electrochemical activity. In this review, we attempt to provide some basic insights into the rational design of Co_3O_4 based materials/composites and their capacitive properties for supercapacitors. The electrochemical advantages of Co_3O_4 as a supercapacitor material are summarized, and many examples are illustrated. The remaining challenges in exploration of Co_3O_4-based materials as efficient electrodes for supercapacitors are also discussed and the future research directions are offered.

Kharade et al [13] used PPy/Co_3O_4 thin film was deposited by electrodeposition method for supercapacitor application. The structural, surface morphological and super capacitive study of PPy/ Co_3O_4 thin film was carried out with the help of X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) study. The structural study of PPy/Co3O4 thin film show cubic crystal structure. The supercapacitive study of electrodeposited PPy/ Co_3O_4 thin film was carried out with the help of cyclic voltammetry (CV), charging-discharging (CD) and electrochemical impedance Spectroscopy (EIS) study. The PPy/ Co_3O_4 thin film gives maximum specific capacitance of 435 F.g-1 at 5 mV.s-1 in 0.5M Na_2SO_4 aqueous electrolyte solution. The PPy/ Co_3O_4 thin film shows coulombic efficiency of 98% while specific energy and specific power was observed to be 80.4 Wh. kg−1 and 20.4 kW kg−1 respectively. From EIS study, PPy/ Co_3O_4 thin film has values of Rs and RCT to be 0.62 Ω and 2.22 Ω respectively at 1V.

3. Objectives of Research / proposed Hypothesis:

- To study the growth of Ni and Mn doped (1% to 5%) Co_3O_4 in thin film form.
- To study various properties such as thickness, optical, electrical properties of as deposited samples.
- To characterize Ni and Mn doped Co_3O_4 thin films for structural, morphological and compositional properties.
- To study electrochemical properties such as cyclic voltammetry and

galvanostatic charge-discharge of Ni and Mn doped Co_3O_4 thin films-based supercapacitors.

- To increase the surface area of active electrodes and hence to enhance the charge storing capacity of Ni and Mn doped Co_3O_4 thin films.

4. Methodology to be adopted

Metal oxide thin film can be prepared by many deposition methods. Some methods are physical while some are chemical in nature. There are various techniques available for deposition of thin films, amongst these, we use chemical deposition method.

a) Growth of good quality Ni and Mn doped Co_3O_4 Thin Films

It is proposed to synthesize Ni and Mn doped Co_3O_4 thin films by chemical method. At initial stages the efforts will be done in order to deposit good quality Ni and Mn doped Co_3O_4 thin films on amorphous and FTO coated conducting glass substrates. Different parameters like concentration of precursor solution, thickness, spray rate, substrate temperature, carrier gas pressure etc. will be optimized to get best quality Ni and Mn doped Co_3O_4 thin films. Then deposited films will be characterized by various characterization techniques.

b) Structural Studies

In this study, deposited Ni and Mn doped Co_3O_4 thin films will be characterized by X- Ray diffraction (XRD) technique. The lattice parameters, crystal structure, interplanar spacing, lattice planes, and crystallite size will be obtained and correlated with the film properties.

c) Morphological and Compositional Studies

In this study the morphology of the prepared Ni and Mn doped Co_3O_4 thin films will be studied by using Scanning Electron Microscopy (SEM) or Transmission Electron Microscopy (TEM). The grain size, surface roughness, porosity will be studied. The compositional analysis of as deposited Ni and Mn doped Co_3O_4 thin films will be studied by using Energy Dispersive Analysis by X-rays (EDAX) technique and Optical Studies.

The optical absorption of Ni and Mn doped Co_3O_4 thin films will be obtained by using UV-Vis spectrophotometer. The coefficient of absorption, bandgap energy (E_g), nature of transition and power factor will be obtained from optical absorption spectra.

d) Electrical Studies

The electrical resistivity measurements of deposited Ni and Mn doped Co_3O_4 thin films will be carried out by using DC two-point probe method. The room temperature electrical resistivity, type of conduction mechanism and activation energies will be determined.

e) Electrochemical Supercapacitor Studies

Performance of Ni and Mn doped Co_3O_4 thin films in supercapacitor will be evaluated with respect to various parameters such as scan rate, specific capacitance, stability cycles and potential range. The Supercapacitive performance of Ni and Mn doped Co_3O_4 thin films will be tested for symmetric and asymmetric modes, for achieving high power density. The galvanostatic charge-discharge mechanism will be studied using chronopotentiometry and the parameters such as specific capacitance, coulomb efficiency, specific energy, and specific power will be calculated. The electrochemical impedance spectroscopy analysis will be carried out in order to find the Rs and Rct values.

5. Importance of Study/Society Application

The Society now a day demands the use and storage of energy on a major scale. The energy stored in the capacitor is nonfaradaic electrical energy. There will be No chemical changes are occurred and hence life cycle of capacitor is unlimited. Super capacitor has less maintenance. Now a day's electrochemical capacitors or supercapacitors are using as storage devices to complement batteries. Supercapacitor has gained more and more attention because of their good advantages such as fast charging and discharging, long life span, simple principle and high-power density compared with lithium batteries and traditional dielectric capacitors. Supercapacitors are used in particular, cars and trains, light weight electronic fuse, backup power sources for calculators, portable electronic devices, foldable electronic devices and wearable mobile phones and many other applications. But these materials are expensive.

Supercapacitors, including Co_3O_4 -based ones, have a comparatively more power density compared to traditional batteries. That means they can deliver and absorb energy rapidly, making them suitable for applications requiring quick bursts of power, such as regenerative braking in vehicles and smoothing out fluctuations in renewable energy systems.

6. Proposed Work Plan / Formulation and Structure of Study

Year wise plan of work and target to be achieved:

Plan of Work and Target to be achieved during First Year

During the first-year a detailed literature survey and collection of good research papers will be studied to gain deep information about work already done and scope of present work. Various chemicals will be procured. A detailed literature survey will be done to get more knowledge of metal oxides and supercapacitors. Efforts will be done in order to synthesize good quality Ni and Mn doped Co_3O_4 thin films by using chemical method.

Plan of Work and Target to be achieved during Second Year

In second year the Ni and Mn doped Co_3O_4 thin films will be characterized by different techniques such as XRD, SEM, AFM and EDAX to study the structural, morphological and compositional properties. The films will be studied for optical properties using UV-Vis spectrophotometer. Grown thin films will be characterized by electrical resistivity measurement. Performance of Ni and Mn doped Co_3O_4 thin films in supercapacitor will be studied by using different parameters such as scan rate, specific capacitance, stability cycles and potential range. The results obtained will be discussed and interpreted. The two progress reports will be sent during the year. Two research papers will be submitted to the reputed journal at the end of this year.

Plan of Work and Target to be achieved during Third Year:

Results which will obtained in second year will be analyzed and published in reputed journals. Also, the outcomes of our research work will be presented in national and international programs such as Seminars, webinars, Workshops, and Conferences set during this year. Once this is over final synopsis will be submitted and after this, thesis will be written. Thesis will be submitted to the university.

7. References:

[1] X. Li, R. Miao, B. Tao, F. Miao, Y. Zang, and P. K. Chu, "Co3O4/MnO2/Co(OH)2 on nickel foam composites electrode with excellent electrochemical performance for supercapacitor," Solid State Sci., vol. 95, p. 105941, Sep. 2019, doi: 10.1016/j.solidstatesciences.2019.105941.

[2] D. Guragain et al., "Electrochemical Performance of Iron-Doped Cobalt Oxide Hierarchical Nanostructure," Processes, vol. 9, no. 12, Art. no. 12, Dec.

2021, doi: 10.3390/pr9122176.
[3] P. S. Gaikar, A. P. Angre, G. Wadhawa, P. V. Ledade, S. H. Mahmood, and T. L. Lambat, “Green synthesis of cobalt oxide thin films as an electrode material for electrochemical capacitor application,” Curr. Res. Green Sustain. Chem., vol. 5, p. 100265, 2022, doi: 10.1016/j.crgsc.2022.100265.
[4] S. K. Jasmin Vijitha, K. Mohanraj, and R. P. Jebin, “Magnetic and electrochemical application of Ru doped Co3O4 thin films,” Chem. Phys. Impact, vol. 6, p. 100183, Jun. 2023, doi: 10.1016/j.chphi.2023.100183.
[5] Mohd. Shkir et al., “Spray pyrolysis developed Nd doped Co3O4 nanostructured thin films and their structural and opto-nonlinear properties for optoelectronics applications,” Opt. Laser Technol., vol. 150, p. 107959, Jun. 2022, doi: 10.1016/j.optlastec.2022.107959.
[6] N. Velhal, T. Yun, J. Ahn, T. Kim, J. Kim, and C. Yim, “Tailoring cobalt oxide nanostructures for stable and high-performance energy storage applications,” Ceram. Int., vol. 49, Oct. 2022, doi: 10.1016/j.ceramint.2022.10.003.
[7] S. K, V. H, and R. Sagar, “Electrical and electrochemical properties of nanostructured Ni and Zn substituted Co3O4 spinels for thermistors and supercapacitor applications,” J. Energy Storage, vol. 52, p. 104871, Aug. 2022, doi: 10.1016/j.est.2022.104871.
[8] S. Aslam, S. M. Ramay, A. Mahmood, G. M. Mustafa, S. Zawar, and S. Atiq, “Electrochemical performance of transition metal doped Co3O4 as electrode material for supercapacitor applications,” J. Sol-Gel Sci. Technol., vol. 105, no. 2, pp. 360–369, Feb. 2023, doi: 10.1007/s10971-022-06008-3.
[9] N. H. M. Zaki et al., “Structural and electronic properties of nickel doped cobalt oxide electrode for supercapacitors: A first principle study,” IOP Conf. Ser. Earth Environ. Sci., vol. 685, no. 1, p. 012029, Mar. 2021, doi: 10.1088/1755-1315/685/1/012029.
[10] S. Lavanya et al., “Enhanced structural, optical, and photo sensing properties of Ni-doped Co3O4 thin films prepared by nebulizer spray pyrolysis method,” Phys. B Condens. Matter, vol. 649, p. 414492, Jan. 2023, doi: 10.1016/j.physb.2022.414492.
[11] L. Abdelhak, B. Amar, B. Bedhiaf, D. Cherifa, and B. Hadj, “Characterization of Mn-Doped Co3O4 Thin Films Prepared by Sol Gel-Based Dip-Coating Process,” High Temp. Mater. Process., vol. 38, no. 2019, pp. 237–247, Jan. 2019,

doi: 10.1515/htmp-2017-0185.

[12] “Recent Progress in Co_3O_4-Based Nanomaterials for Supercapacitors - Lu - 2023 – Chem Nano Mat Wiley Online Library.” https://onlinelibrary.wiley .com/ doi/abs/10.1002/cnma.202200537 (accessed Aug. 24, 2023).

[13]P. Kharade et al., Structural, Morphological and Supercapacitive Performance of Electrodeposited PPy/Co_3O_4 Thin Film. 2021.

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